H.M. FACTORY INSPECTORATE
MINISTRY OF LABOUR AND NATIONAL SERVICE

Methods for the Detection of Toxic Substances in Air
Booklet No. 8

PHOSGENE

LONDON
HER MAJESTY'S STATIONERY OFFICE
FOUR SHILLINGS NET

H.M. FACTORY INSPECTORATE
MINISTRY OF LABOUR AND NATIONAL SERVICE

Booklet on Methods for the Detection of Toxic Substances in Air

The circumstances in which the substances covered by this series of booklets are commonly encountered in industry are mentioned below. Each booklet contains details of a test capable of detecting concentrations of the poison down to, and in most cases below, the danger limit. A high degree of accuracy is not claimed for any of these methods—when an atmosphere is being certified as "free from danger", an ample factor of safety must always be allowed, and in such circumstances, extreme accuracy is not necessary.

Booklet No. 1. Hydrogen Sulphide.

Hydrogen sulphide (sulphuretted hydrogen) may be met in many industries, including artificial silk works, chemical works, gas works and coke ovens, by-product works and tar distillation works, and oil refineries. It may also occur in sludge pits, sewers and cesspools, and at sewage works. **4s. 6d.** (*post 2d.*)

Booklet No. 2. Hydrogen Cyanide.

Hydrogen cyanide (prussic acid) is used mainly in the fumigation of ships and buildings. It is a potential hazard wherever cyanides are used in quantity, as in electro-plating and heat treatment of metals. **5s. 6d.** (*post 2d.*)

Booklet No. 3. Sulphur Dioxide.

Sulphur dioxide is used in many industries, notably sulphuric acid manufacture, oil refining, and glucose manufacture. Its excellent reducing and bleaching properties are made use of in textile, paper and other industries. **3s. 6d.** (*post 2d.*)

Booklet No. 4. Benzene Vapour.

Benzene (in commercial grades, Benzol) is produced during the carbonisation of coal, and is recovered in tar and benzene distillation plants. It is used in the manufacture of explosives and dyestuffs, and as a solvent for lacquer, paint, varnish and rubber. The vapour may be met wherever benzene is used as a solvent. **1s. 6d.** (*post 2d.*)

Booklet No. 5. Nitrous Fumes.

The term "nitrous fumes" embraces mixtures of varying compositions of the higher oxides of nitrogen. Such fumes may be met in any nitration process, in the manufacture of sulphuric acid by the chamber process, in engraving and pickling in nitric acid, and in the use of nitrate baths for the heat treatment of metals. Fatal concentrations of nitrous fumes have been produced in confined spaces during the heating of large masses of metal by oxy-acetylene flames in shipbuilding and repairing. **1s. 6d.** (*post 2d.*)

Booklet No. 6. Carbon Bisulphide Vapour.

Carbon bisulphide is mainly used in the manufacture of artificial silk (viscose) and certain chemicals (xanthates). **9d.** (*post 2d.*)

Booklet No. 7. Carbon Monoxide (Revised Edition).

Carbon monoxide results from the incomplete combustion of carbonaceous materials and is therefore produced in a wide variety of processes and conditions. It is encountered in concentrations which may be dangerous in many industrial works, and particularly in steelworks, foundries, gasworks, coke oven plant, and wherever gas producers and water gas plant are operated. It is perhaps most dangerous when formed unknowingly, as by the improper use of gas water heaters (geysers), boilers, braziers; in mine explosions ("after damp"); in the smoke from fires; and in the exhaust gas from petrol engines. **9d.** (*post 2d.*)

(*Continued on outside back cover*)

H.M. FACTORY INSPECTORATE

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PHOSGENE

LONDON

HER MAJESTY'S STATIONERY OFFICE

1939: Reprinted 1958

FOREWORD

The present booklet is a revised reprint of the original booklet on Phosgene published in 1939 and sponsored by the Department of Scientific and Industrial Research.

Under Regulation 7 of the Chemical Works Regulations, 1922, before any person enters for any purpose except that of rescue, any vessel or other place that may contain dangerous gas or fume, the vessel or place must be personally examined by a responsible person appointed by the occupier, and the appointed person must certify in writing whether the place is free or not free from danger.

White mice and birds have been used for the purpose of testing for the presence of dangerous gas and fume. Though this method may, in certain situations, be effective for carbon monoxide, experience has shown that it cannot always be relied upon for other important gases and vapours encountered in industry and that there is a need for simple and rapid chemical or other methods for determining low concentrations of dangerous gases, such as may occur in various circumstances in chemical work. The matter was discussed by the Association of British Chemical Manufacturers with the Home Office in 1932, and as a result arrangements were made by the Department of Scientific and Industrial Research, at the request of the Home Office and with the financial and technical co-operation of the Association of British Chemical Manufacturers, for a series of tests to be developed by the Chemical Defence Research Department. The tests devised were described in twelve booklets which were published between 1937 and 1940; they covered the following gases and vapours:

Aniline	Hydrogen cyanide
Arsine	Hydrogen sulphide
Benzene	Nitrous fumes
Carbon bisulphide	Organic halogen compounds
Carbon monoxide	Phosgene
Chlorine	Sulphur dioxide

Originally, this series of tests was worked out to help the chemical industry to comply with the Chemical Works Regulations, 1922. Requirements similar to those already in force for chemical works were imposed on all other works in the Factories Acts of 1937 and 1948, so that the usefulness of this series has been much extended. The methods are also of value in work-rooms where the general atmosphere is liable to contamination, and in this connection it is intended to cover airborne solids as well as gases and vapours.

In most cases, chemical methods involving colour changes were adopted as best suited for the purpose in view. Each test was carefully standardized in the laboratory, and tested under practical conditions in actual works. While the information contained in the booklets describing the tests is addressed primarily to responsible works officials, medical officers, chemists and other persons in charge of chemical plant, the tests themselves have been made as simple and straightforward as possible in order that they can be operated, given the necessary materials, by comparatively unskilled personnel. They can be elaborated or modified to a certain extent to suit particular conditions, provided that the fundamental conditions laid down for the tests are not altered in any way. In this connection it must be remembered, however, that the primary

object of the tests is not to obtain an extreme degree of accuracy, but to give a rapid indication of the relative safety of the atmosphere. A result which is close to the danger limit should always be regarded as indicating that conditions are dangerous.

It must be borne in mind that each of the above tests will indicate only the presence or absence of the specific poison, and in cases where any other poison is liable to occur, the relevant test for it must be applied before the atmosphere is adjudged as safe to breathe. **Further, none of the tests will indicate the danger which exists in cases where the oxygen content of an atmosphere is dangerously deficient.**

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19 St. James's Square,
London, S.W.1.

NOTE

It should be emphasized that the object of the tests is to give a rapid determination of the relative safety of the atmosphere, and not to give an accurate estimation of the concentration of dangerous vapour.

The envelope inside the back of the cover contains a copy of the standard stains produced on *p*-dimethylaminobenzaldehyde-diphenylamine paper. Further copies of these stains can be obtained from H.M. Stationery Office at the price of 3s. 0d. (post free 3s. 2d.)

PHOSGENE

OCCURRENCE

PHOSGENE (carbonyl chloride) is made especially for use in certain industrial processes, particularly in the dyestuffs, organic-chemical and pharmaceutical industries. It is also used in the manufacture of several metallic oxides. It may be encountered in dangerous concentrations in works in these and other industries. Phosgene may also occur as a decomposition product of trichlorethylene and of carbon tetrachloride (used for example in some forms of fire extinguishers).

POISONOUS EFFECTS

Phosgene has a strong " musty " smell and produces lachrymation, but is not so immediately irritant to the senses as chlorine. It is, however, a much more deadly gas than chlorine. Atmospheres containing concentrations of phosgene only just detectable by smell or lachrymation and consequently easily " tolerable," may prove fatal.

Phosgene produces very severe damage to the walls of the alveoli (air cells) of the lungs, followed by the escape of watery fluid from the blood into the air sacs of the lungs (pulmonary oedema). If this is severe, the patient is slowly asphyxiated, because the fluid prevents the blood in the lungs from taking up the oxygen from the air breathed. In other words, the affected person is " drowned " in his own secretions. As the amount of fluid which escapes from the damaged capillaries into the air cells depends largely upon the blood pressure, it is obviously imperative that absolute rest after gassing is necessary. There is always a period of some hours delay before the person who has breathed a dangerous dose of phosgene becomes acutely ill. The immediate symptoms following a dangerous or even a fatal dose of phosgene may be comparatively mild—such as a little coughing, tightness of the chest, and some lachrymation. From these mild symptoms the subject may appear to recover fairly rapidly, and appear quite well, only to become progressively breathless and acutely ill some hours later, because of the onset of severe oedema of the lungs.

The insidious character of this gas is, therefore, in part due to its relatively non-irritant character, by an apparently rapid recovery from the initial symptoms, and the delayed onset of an acute illness.

The following table shows the effect of known concentrations for various periods of exposure:

Concentration of Phosgene in air			
Parts per million by vol. (approximately)	*mg./litre (approximately)*	*Duration of exposure*	*Effects*
160	**0.70**	2 minutes	Very serious lung injury in all cases with a death rate of about 50 per cent.*
33	**0.14**	2 minutes	Very dangerous. Risk of serious lung injury.*
5	**0.02**	30 minutes	Probably fatal.†
2	**0.008**	" Prolonged "	Dangerous to life.†
1	**0.004**	" Prolonged "	Maximum amount permissible.‡

*British data. †Lehmann, Flury, and Zernik (1931).
‡Henderson and Haggard (Noxious Gases), 1927.

Continuous work must not be permitted in an atmosphere in which the presence of phosgene can be detected by the test described below.

METHODS OF DETECTION

One simple method of detecting low concentrations of phosgene is by the use of a test-paper containing diphenylamine and *p*-dimethylaminobenzaldehyde. The gas produces a yellow or orange stain on the paper and an indication of its presence may be obtained even at concentrations of the order of 1 in 1,000,000 (0.004 mg/1.) by exposing the paper for a few minutes.

This test has been adopted as the standard method for the detection of phosgene in industry. It has been made quantitative by drawing known volumes of the atmosphere under test through a definite area of test-paper by means of a hand pump of specified capacity. From the number of strokes of the pump required to produce stains of certain intensity, the concentration present is obtained by reference to a colour chart. In this way, concentrations down to 1 in 1,000,000 (0.004 mg/1.) are readily determined with not more than 85 strokes of the pump.

It must be noted, however, that the stains produced are only transient, and that the sampling and comparison of the stains must therefore be carried out as rapidly as possible.

The test-papers are sensitive also to hydrogen chloride and chlorine. Traces of these gases can, however, be removed from the sample by drawing it first through a guard tube containing pumice granules impregnated with sodium thiosulphate and sodium iodide. These react with the interfering gases, but allow any phosgene to pass through and react with the test-paper.

INSTRUCTIONS FOR CARRYING OUT THE TEST FOR PHOSGENE

GENERAL

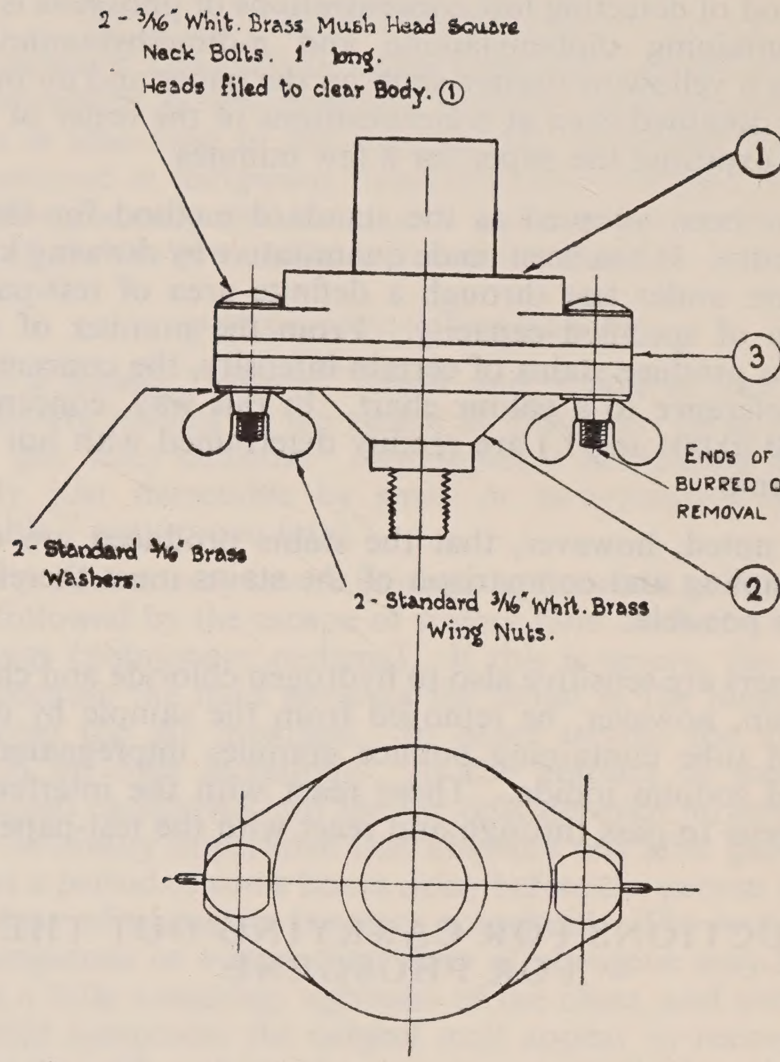
Although the test is simple and accurate, it should preferably be carried out only by a responsible person appointed by the occupier, as for example the person appointed under Regulation 7 of the Chemical Works Regulations, 1922, in the case of entry into vessels. All necessary steps should be taken for the protection of the person carrying out the tests.

In determining the concentration of phosgene in a workroom, samples should be taken at a point closely adjacent to the workers, as an average sample for the whole workroom may give misleading figures of the concentrations actually inhaled.

In determining the concentration of phosgene in the atmosphere inside an enclosed space prior to the entry of a workman, it may be insufficient to do only one test. When there is any chance of the concentration inside the space rising, no person should enter the space unless he is wearing breathing apparatus as required under Section 27 of the Factories Act, 1937 and Regulation 7 of the Chemical Works Regulations, 1922.

APPARATUS

The atmosphere being tested shall be sampled by means of a hand exhausting pump with a barrel of approximately 1.25 in. bore and a capacity of 126ml; the inlet end of the pump should be screwed internally to take a spigot screwed 7/16 in. Whit., 14 T.P.I. on 0.437 in. diameter. The pump may be fitted, if desired, with a device for counting the number of strokes made.



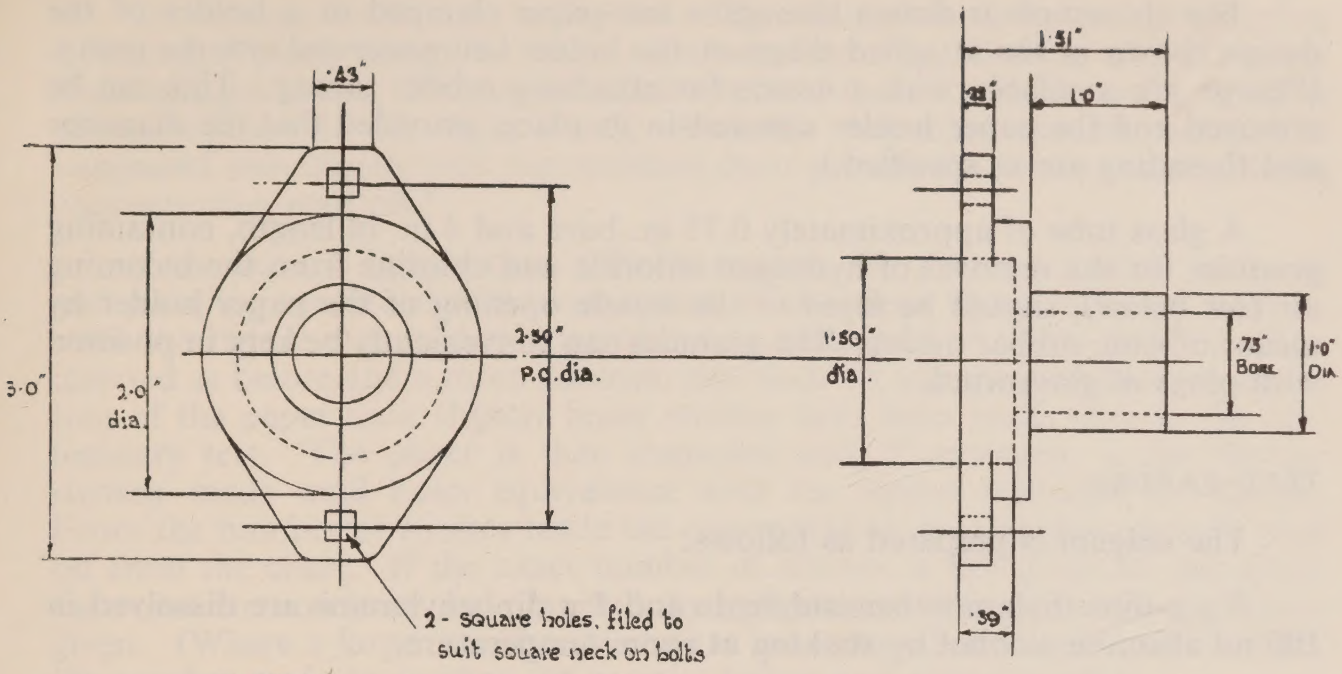
ASSEMBLY

NOTE

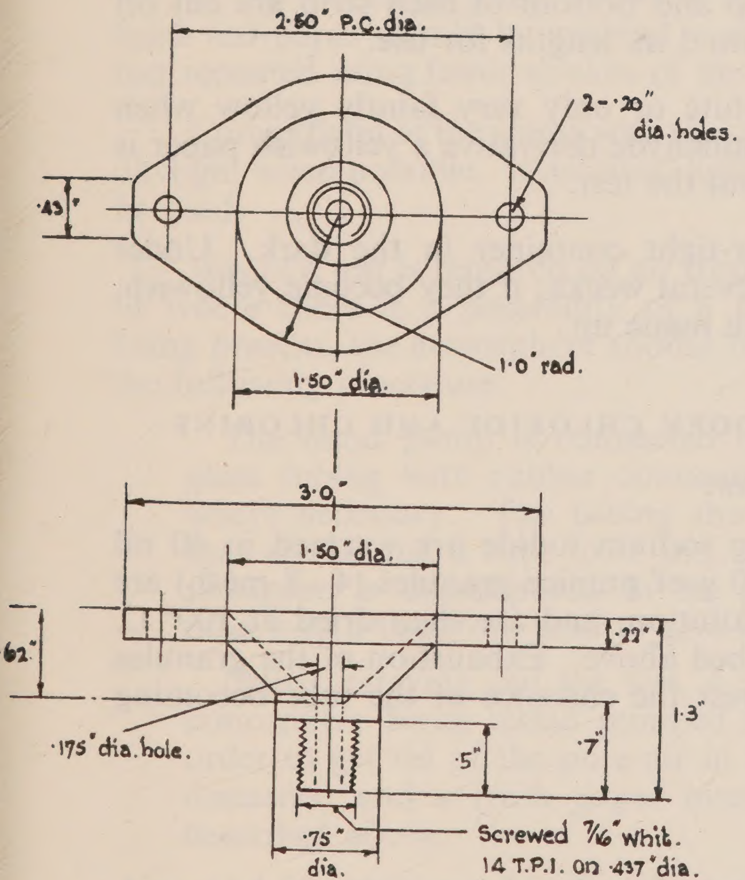
All dimensions must be worked to with reasonable approximation.

HAND PUMP ATTACHMENT FOR

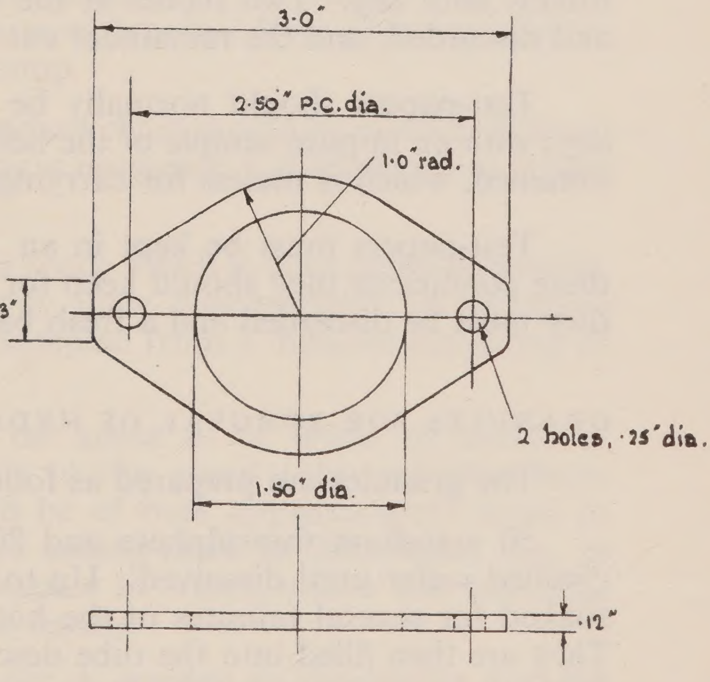
(SCALE:



BODY: 1 OFF, ALUMINIUM, TO BE MACHINED ALL OVER



COVER: 1 OFF, ALUMINIUM, TO BE
MACHINED ALL OVER



PACKING
1 OFF

WASHER
RUBBER

DETECTION OF TOXIC ATMOSPHERES
ALF SIZE)

The air sample is drawn through a test-paper clamped in a holder of the design shown in the attached diagram, the holder being screwed into the pump. (Pumps are available with a nozzle for attaching rubber tubing. This can be removed and the paper holder screwed in its place, provided that the diameter and threading are as specified.)

A glass tube of approximately 0.75 in. bore and 4 in. in length, containing granules for the removal of hydrogen chloride and chlorine from the incoming air (*see* below), should be fitted to the nozzle opening of the paper holder by means of wide rubber tubing. The granules can conveniently be kept in position with plugs of glass wool.

TEST-PAPERS

The reagent is prepared as follows:

5 g *p*-dimethylaminobenzaldehyde and 5 g diphenylamine are dissolved in 100 ml absolute alcohol by shaking at room temperature.

The chemicals used in preparing this solution should be of " Reagent " quality.

The test-papers are prepared from Whatman No. 1 filter paper, cut into strips 2 in. in width. The strips are immersed in the reagent for 1 minute and then suspended vertically in the dark in air free from phosgene or any acid fumes, until dry. Two inches at the top and bottom of each strip are cut off and discarded, and the remainder cut into 3 in. lengths for use.

Test-papers should normally be white or only very faintly yellow when dry; with an impure sample of the benzaldehyde derivative a yellowish paper is obtained, which is useless for carrying out the test.

Test-papers must be kept in an air-tight container in the dark. Under these conditions they should keep for several weeks; if they become yellowish, they must be discarded and a fresh batch made up.

GRANULES FOR REMOVAL OF HYDROGEN CHLORIDE AND CHLORINE

The granules are prepared as follows:

50 g sodium thiosulphate and 20 g sodium iodide are warmed in 40 ml distilled water until dissolved. Up to 70 g of pumice granules (4 - 8 mesh) are soaked for several minutes in the hot solution, and are then dried at 100° C. They are then filled into the tube described above. Exhaustion of the granules in the tube is shown by the layers nearest the entrance of the tube becoming brown.

METHOD

Before a test is carried out, the valves of the hand pump should be tested. The inlet should be closed with the finger and the pump handle drawn out a few inches. On being released, the pump handle should spring back to its original position; if it does not, the valves should be renewed. Ordinary transparent wrapping, *e.g.*, cellophane, will be found a satisfactory material for the valves.

The paper holder is screwed into the pump, a strip of test paper inserted, in an atmosphere free from phosgene, and the wing nuts on the holder tightened. The apparatus should again be tested for leaks as described above by closing the inlet of the paper holder.

To obtain a preliminary indication of the atmosphere to be tested, 10 strokes of the hand pump should be made, slowly and steadily, allowing approximately 3 seconds per stroke. The paper is then removed from the holder so as to allow of examination of the stain, if any, obtained. Any stain obtained should be compared *immediately* with the standard chart provided, and the corresponding concentration read off.*

If the stain is lighter than either standard, the paper is quickly replaced and pumping continued with examination of the paper about every ten strokes, until the lighter standard is approximately obtained. A fresh paper is then inserted as before and a more accurate test made by pumping without examination of the paper until slightly fewer strokes have been made than in the preliminary test. The paper is then inspected and, if necessary, a few further strokes made until exact equivalence with the lighter standard is reached. From the number of strokes made the concentration present may then be read off from the chart. If the exact number of strokes is not given on the chart, the concentration may be obtained by proportion from the nearest figures given. (Where a larger number of strokes is employed, it is advisable to check the number made by reading the counter before and after the test.)

If in the preliminary test with ten strokes a stain is obtained intermediate between the two standards, immediate precautionary measures must be taken. Pumping may then be continued until the deeper standard is reached, and a confirmatory test made as above.

If the preliminary test shows a stain deeper than the deeper standard, a fresh test-paper should be inserted in an atmosphere free from phosgene and the test repeated using fewer strokes of the pump.

Comparison of the stains with the standard chart should be made in diffused daylight when possible. If artificial lighting is necessary, a daylight lamp should be used.

Where a test is required on air from a space which is not readily accessible, or where there is a possibility of a highly toxic concentration of phosgene being present, the atmosphere should be sampled from a distance according to the following procedure:

> The hand pump is connected to the space to be tested by means of glass tubing with rubber connections to the guard tube and elsewhere, where necessary. The tubing should be of bore approximately equal to that of the guard tube (0.75 in.). All tubing must be thoroughly dry, as phosgene is decomposed in the presence of water, and a wet sampling tube would therefore tend to give low results.
>
> Before carrying out the test, a paper is inserted in the holder and the atmosphere being tested pumped through it until a stain is obtained, in order to get rid of the pure air in the tubing. This paper is removed and discarded and a fresh paper inserted. The test is then carried out as described above.
>
> An alternative method, where it can be used, is to attach the paper-holder to the end of several lengths of $\frac{1}{2}$-inch metal gas tubing, making sure the joints are gas-tight, and to lower it into the atmosphere to be tested. Since in this method the gas passes through, and is absorbed by,

*There are alternative methods of comparing the colours obtained, *e.g.* by means of a comparator using coloured glasses as standards, a photo-electric colorimeter, or an optical density meter. Provided that the standards employed have been properly calibrated and are used according to standard instructions, such methods can be quite satisfactory and may have advantages of permanence and accuracy of standards, and of simplicity of technique. They are likely to be particularly applicable in works where a large number of tests is carried out.

the test-paper before entering the sampling tube, the necessity for using glass tubing for the latter, and for preliminary pumping to clear the pure air from the tube, is thereby avoided. When this method is used, particularly if the holder is likely to remain in the atmosphere for some minutes, or if the test is being made in a strong current of air, it is advisable to place a plain dry filter paper in front of the test-paper in the holder, separated from it by the rubber washer. This avoids the possibility of the paper reacting with the gas during the preliminary operations before pumping is commenced.

FIRST AID

The following first-aid treatment of a patient who has inhaled phosgene is based on the importance of rest in preventing lung oedema from occurring. This rest must be as complete as possible, both physical and mental. It must also be remembered that the patient may feel comparatively well and may regard treatment as quite unnecessary.

Remove the patient from the toxic atmosphere.

Make him lie down and keep him lying down.

Keep him warm with hot-water bottles, to prevent muscular activity by shivering. Warm drinks may be given if necessary, but no alcoholic stimulants.

Convey him to his home, or better still to a hospital, *still lying down*, for medical treatment. He must not be regarded as having escaped injury until at least 24 hours have elapsed following the inhalation of phosgene.

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and published by Her Majesty's Stationery Office.

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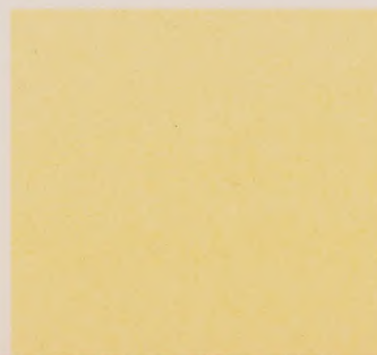
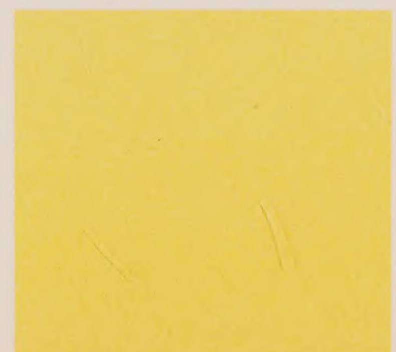
6495-(M.F.P.)

DETECTION OF PHOSGENE

STANDARD STAINS PRODUCED ON *P*-DIMETHYLAMINOBENZALDEHYDE-DIPHENYLAMINE TEST PAPERS

Concentration			
p.p.m.	*mgs./litre*	*No. of Strokes*	*No. of Strokes*
100	0.41	1	4
50	0.21	2	8
33	0.14	3	12
20	0.083	5	20
10	0.041	10	40
7	0.028	15	60
4	0.015	25	—
2	0.009	40	—
1.5	0.006	60	—
1.0	0.004	85	—





**As the colours
of the chart
might be subject to
fading in sunlight,
the chart should be
kept in this pocket
when not in use**

Booklet No. 8. Phosgene.

Phosgene (carbonyl chloride) is used in the manufacture of certain chemicals (*e.g.*, di- and tri-phenyl methane dyestuffs) and may result from the decomposition of chlorinated hydrocarbons (*e.g.*, trichlorethylene, carbon tetrachloride) in contact with a hot surface. **4s.** (*post* 2*d*.)

Booklet No. 9. Arsine.

Arsine (arseniuretted hydrogen) is always produced when hydrogen is liberated in solutions containing arsenites. Appreciable concentrations of the gas may be produced even from traces of arsenic present as impurities. Danger arises when an acid (*e.g.*, hydrochloric, sulphuric) containing such impurities is in contact with iron, zinc or similar metal. **3s.** (*post* 2*d*.)

Booklet No. 10. Chlorine (Revised Edition).

Chlorine is widely used for its bleaching and sterilizing properties (*e.g.*, in paper and textile industries and in the purification of water supplies). It may be liberated when hypochlorites come, unintentionally perhaps, into contact with acids. **9d.** (*post* 2*d*.)

Booklet No. 11. Aniline Vapour.

Aniline is made by the reduction of nitrobenzene. The risk of poisoning by aniline vapour occurs mainly in the manufacture and use of aniline dyestuffs. **9d.** (*post* 2*d*.)

Booklet No. 12. Organic Halogen Compounds.

Certain of the organic halogen compounds are widely used as solvents, in degreasing and dry cleaning, in fat extraction, and in the paint and rubber industries. Others are used for purposes such as refrigeration, disinfestation, and fire-fighting, and in chemical manufacturing processes. **9d.** (*post* 2*d*.)

Booklet No. 13. Mercury in Air.

Metallic mercury is used in the manufacture of certain electrical and scientific equipment. Oxides of mercury are used in some surgical dressings and certain types of dry-cell batteries.

Organic mercury compounds are used as seed dressings and fungicides and mercury fulminate is a detonating agent. **3s.** (*post* 2*d*.)

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